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(54) **Title of the Invention : Water Repellent Reflection Reduction Glass**

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(54) [Title of the Invention] **Water Repellent Reflection Reduction Glass**

(57) [Abstract]

[Objective] This is to obtain a water repellent reflection reduction glass, especially one for automobile windows, which possesses water and oil repellence and soil resistance properties, reflection reduction, and to demonstrate this performance further, excels in bonding property, scratch resistance property, and weatherability, maintains its performance in these for a long period, and can sufficiently cope with the attachment of water and soiling with simple wiping without losing its optical characteristics.

[Construction] With respect to the reflection reduction glass which is made to reduce the reflection of a glass surface by layering thin oxide membranes possessing differing refractive indexes on one side of a glass substrate, this is the water repellent reflection reduction glass which is made by forming a SiO_2 thin membrane or a mixed oxide thin membrane of SiO_2 and other oxides possessing a refractive index of less than 1.5 where a silane compound containing polyfluoroalkyl group is bonded to the side opposite the side onto which said thin membranes have been laminated.

[Claims]

[Claim 1] With respect to the reflection reduction glass which is made to reduce the reflection of a glass surface by layering thin oxide membranes possessing differing refractive indexes on one side of a glass substrate, this is the water repellent reflection reduction glass which is characterized by being made by forming, on the side opposite the side onto which said thin membranes have been laminated, a SiO_2 thin membrane or a thin mixed oxide membrane of SiO_2 and other oxides possessing a refractive index n of less than 1.5, onto the surface of which a silane compound containing polyfluoroalkyl group is bonded.

[Claim 2] The water repellent reflection reduction glass described in Claim 1 which is characterized by the refractive index n of the aforementioned SiO_2 thin membrane or the thin mixed oxide membrane being less than 1.47.

[Claim 3] The water repellent reflection reduction glass described in Claims 1 ~ 2 which is characterized by the aforementioned silane compound containing the polyfluoroalkyl group being made with a single to a few tens of molecular layers.

[Claim 4] The water repellent reflection reduction glass described in Claims 1 ~ 3 which is characterized by the aforementioned water repellent reflection reduction glass being glass where at least two glass substrates are adhered having an intermediary membrane or an intermediary membrane shaped material possessing a single or various functional properties between them.

[Claim 5] With respect to the aforementioned water repellent reflection reduction glass, the water repellent reflection reduction glass described in Claims 1 ~ 4 which is characterized by the aforementioned laminated oxide thin membrane layer being made of a thin membrane layer which reduces the reflective index of entry light possessing a specified incident angle the most.

[Claim 6] With respect to the aforementioned water repellent reflection reduction glass, the water repellent reflection reduction glass described in Claims 1 ~ 5 which is characterized by the aforementioned specified incident angle being $40 \sim 80^\circ$ and the reflective index reduction rate being $4.5 \sim 7\%$ with the visible light reflective index.

[Claim 7] With respect to the aforementioned water repellent reflection reduction glass, the water repellent reflection reduction glass described in Claims 1 ~ 6 which is characterized by the SiO_2 thin membrane or the mixed thin oxide membrane of SiO_2 and other oxides, on the surface of which a silane compound containing a polyfluoroalkyl group is covered, possessing a refractive index n of $1.43 \sim 1.47$ and a membrane thickness of $105 \sim 130 \text{ nm}$.

[Claim 8] The water repellent reflection reduction glass described in Claims 1 ~ 7 which is characterized by the aforementioned water repellent reflection reduction glass being the front window of an automobile made of layered glass, where the thin oxide membrane layer which reduces reflection faces the interior of the vehicle and where the SiO_2 thin membrane or the thin mixed oxide membrane of SiO_2 and other oxides, on the surface of which a silane compound containing the polyfluoroalkyl group is covered, faces the exterior of the vehicle.

[Claim 9] The water repellent reflection reduction glass described in Claims 1 ~ 8 which is characterized by the various thin oxide membranes of the aforementioned reflection reduction glass being formed using the sol-gel method where more than one kind of organic metal compound is used as the starting raw material.

[Claim 10] The water repellent reflection reduction glass described in Claims 1 ~ 9 which is characterized by the SiO_2 thin membrane or the mixed oxide thin membrane of SiO_2 and other oxides, on the surface of which a silane compound containing a polyfluoroalkyl group is covered, being made by first forming the SiO_2 thin membrane or the mixed oxide thin membrane of SiO_2 and other oxides on the surface of a glass substrate at a treatment temperature of more than 400°C , and thereafter coating, or coating and drying the silane compound containing the polyfluoroalkyl group onto said oxide thin membrane surface at a temperature of less than 400°C .

[Claim 11] The water repellent reflection reduction glass described in Claims 1 ~ 10 which is characterized by the aforementioned oxides which mix with SiO_2 being whichever of or a mixture of TiO_2 , ZrO_2 , Al_2O_3 , B_2O_3 , SnO_2 , In_2O_3 , and TaO_3 .

[Claim 12] The water repellent reflection reduction glass described in Claims 1 ~ 11 which is characterized by the aforementioned oxide thin membrane layer which is formed on the surface of the glass substrate being 2 or 3 layers.

[Claim 13] The water repellent reflection reduction glass described in Claims 1 ~ 12 which is characterized by the uppermost layer of the aforementioned oxide thin membrane layers being the same membrane as the SiO_2 thin membrane or the mixed oxide thin membrane of SiO_2 and other oxides which is formed on the side opposite the said oxide thin membrane layer.

[Detailed Explanation of the Invention]

[0001] [Industrial Application Area]

This invention is to present a water repellent reflection reduction glass which reduces the reflection of one side of a glass substrate, is used for vehicles, construction, and in general industry, possesses an effect of reducing the mirroring phenomenon during driving of a dashboard to the front glass which has been attached at a specified slope angle to the dashboard, simultaneously causes the exterior of a vehicle to possess water repellence or at least possesses an effect of making water and soiling difficult to attach to the surface, makes the said membrane possess a reflection reduction performance or/and strengthens the reflection reduction in its entirety, and increases the transmission property in the direction of vision without losing its optical characteristics, thereby providing improvements in safety, especially for vehicles.

[0002] [Prior Technology and Problems]

Conventionally, drivers and passengers have desired that they be provided with more safety against oncoming vehicles and excellent riding comfort and environment with an improvement in clear visibility by lowering the reflective index of the glass substrate, and utilizing multiple layer interference by laminating oxide membranes possessing differing refractive indexes onto a glass substrate. Among them, the so-called multiple layer membranes low reflective glass is well known and is used extensively for construction, industry, and vehicles.

[0003] Especially, with the conventional low reflection property used for front glasses which are attached at a specified slope angle, the objective has been to reduce the frontal reflected light, but in opposition to the slanted entry light which has an incident angle in relation to the perpendicular line of the aforementioned front glass surface of more than, for example, $50^\circ \sim 70^\circ$, its reflection reduction effect has been halved; accordingly, the frontal view

recognition of a driver is reduced due to reflection from the dashboard or nearby materials off the front glass, and consequently, safety is reduced.

[0004] Against this, for example, a method for the formation of reflection preventive coatings was disclosed in Tokkyo Kokai No. J.P. Hei. 3 - 17601; also, as for that where two layers of reflection preventive membranes are laminated, for example, a transparent panel which possesses an electric conductive reflection preventive membrane was disclosed in Tokkyo Kokai No. J.P. Sho. 64 - 70701; further, as for that where three layers of reflective preventive membranes are laminated, for example, a transparent low reflective panel was disclosed in Tokkyo Kokai No. J.P. Sho. 61 - 189501.

[0005] However, with these multiple layered membrane low reflective glasses, their refractive index and membrane thickness have been very precisely calculated in order to realize the desired optical characteristic; if they were outside the prescribed membrane construction, the targeted optical characteristics could not be obtained, and in addition, when hand sweat, oil, and water stains were attached, because these soilings acted as new thin membranes formed on the low reflective membrane, the same problems were caused.

[0006] When this happens, the part where soiling is attached fails in optical design, its reflective index is increased, and it becomes very visible relative to the surrounding proper low reflective part; this causes a loss in its see-through visibility and beauty.

[0007] Especially, when oily soils such as fingerprints are attached, unless they are wiped off completely with solvents such as alcohol, its appearance remains permanently damaged, and the use of solvents cannot be said to be good for the environment. Also, there are other problems such as wiping trace marks being left.

[0008] Among those described above, for example, while a low reflective index glass possessing soiling preventive property was disclosed in Tokkyo Koho No. J.P. Hei. 3 - 23493, it was that where a two layered membrane is formed comprised of a thin membrane possessing a refractive index of more than 1.60, and it was made of a condensate containing metal oxide on the surface of glass and a thin membrane made of a condensate of fluorosilicone contained compound possessing a polyfluorocarbon chain having a carbon number of more than two where fluorine atoms were bonded to the said thin membrane, but this is that where F-alkylsilane and Si-alcoxide are mixed and where this hybrid solution is used in an attempt to obtain water repellence and low reflective properties simultaneously.

[0009] [The Problems Solved by the Invention]

As described in, for example, the aforementioned Tokkyo Kokai No. J.P. Hei. 3 - 17601, the method of forming a coating possessing a concentration gradient of light metal fluorinated material to the thickness of the coating using sol-gel technology is accompanied by very complicated processes and is difficult to be said to be economical with good productivity and high efficiency. Also, with respect to those described in, for example, Tokkyo Kokai No. J.P. Sho. 64 - 70701 and Tokkyo Kokai No. J.P. Sho. 61 - 189501, they have difficulty in obtaining a reflective reduction effect which is stable and sufficient against the aforementioned specific slanted entry light, and both cannot be said to have the durability necessary for vehicle usage. Further, that described in Tokkyo Koho No. J.P. Hei. 3 - 23493 has a problem in that only those which are low in terms of the hardness and strength of the uppermost membranes can be obtained because the last heating temperature is less than 400°C, for example, about 160 ~ 200°C, to prevent the decomposition of F-alkylsilane.

[0010] Further, this is the reflection reduction effect manifested when a oxide thin membrane possessing 2 ~ 3 layers is formed on only one side of a glass substrate which is in a range of 4 ~ 6%; it is very effective compared to untreated glass, but a higher reflection reduction effectiveness is desired if possible. However, for this, not only can an improvement in performance not be expected even if further thin layers are laminated on the same side, but also, as the number of laminated thin layers increases, the durability of the membrane becomes insufficient, the consistency of the thin membrane layer decreases, the manufacturing process becomes complicated and the cost increases even if a light improvement of less than 1% can be seen.

[0011] [Method for Solving the Problem]

This invention is involved with such conventional problems and with strengthening the reflective reduction effect manifested when 2 ~ 3 layers of oxide thin membrane layers are formed on only one side of a glass substrate without increasing the lamination number of thin membrane layers on the same side; this invention has its objective in improving the performance an approximately additional 0.5 ~ 2.0% compared to the case of only the 2 ~ 3 layers of oxide thin membrane layers by forming a thin membrane possessing a refractive index of less than 1.50, which is lower than the refractive index $n = 1.51 \sim 1.53$ of the most commonly used soda lime silicate glass, on the side opposite the side on which the said thin membrane layers have been formed, thereby reducing the reflection (called the backside reflection) of the side opposite the light passing through the said 2 ~ 3 layers of oxide thin membrane layers and entering into the glass. Furthermore, this invention presents a water repellent reflection reduction glass which becomes multiply functional, possessing a

strengthened reflection reduction effect, water repellence, and soil preventive effect with the introduction of a polyfluoroalkyl group possessing fluorine atoms to this thin membrane.

[0012] That is to say, with respect to the reflection reduction glass which causes the reflection of a glass surface to be reduced by layering thin oxide membranes possessing differing refractive indexes on one side of a glass substrate, this invention is the water repellent reflection reduction glass which is characterized by being made by a SiO_2 thin membrane or a thin mixed oxide membrane of SiO_2 and other oxides possessing a refractive index n of less than 1.5, on the surface of which a silane compound containing a polyfluoroalkyl group has been bonded, being formed on the side opposite the side on which the said thin membranes have been laminated.

[0013] And, this invention is the water repellent reflection reduction glass described above which is characterized by the refractive index n of the aforementioned SiO_2 thin membrane or the mixed oxide thin membrane of SiO_2 and other oxides being less than 1.47. And, this invention is the water repellent reflection reduction glass which is characterized by the aforementioned silane compound containing the polyfluoroalkyl group being made with a single to a few tens of molecular layers.

[0014] Further, this is the water repellent reflection reduction glass described above which is characterized by the aforementioned water repellent reflection reduction glass being glass where at least two glass substrates are adhered by having an intermediary membrane or an intermediary membrane shaped material possessing a single or various functional properties between them.

[0015] Further, with respect to the aforementioned water repellent reflection reduction glass, this is the water repellent reflection reduction glass which is characterized by the aforementioned layered oxide thin membrane layer being made of a thin membrane layer where its reflective index is reduced the most against entry light possessing a specified incident angle.

[0016] Furthermore, with respect to the aforementioned water repellent reflection reduction glass, this is the water repellent reflection reduction glass described above which is characterized by the aforementioned specified incident angle being $40 \sim 80^\circ$ and the reflective index reduction rate being $4.5 \sim 7\%$ with the visible light reflective index.

[0017] Furthermore, with respect to the aforementioned water repellent reflection reduction glass, this is the water repellent reduction glass described above which is characterized by the

SiO₂ thin membrane or the mixed oxide thin membrane of SiO₂ and other oxides, on the surface of which a silane compound containing a polyfluoroalkyl group has been covered, possessing a refractive index n of 1.43 ~ 1.47 and a membrane thickness of 105 ~ 130 nm.

[0018] Also, this is the water repellent reflection reduction glass described above which is characterized by the aforementioned water repellent reflection reduction glass being the front window of an automobile made by layered glass, and where the thin oxide membrane layer which reduces reflection faces the interior of the vehicle and the SiO₂ thin membrane or the thin mixed oxide membrane of SiO₂ and other oxides, on the surface of which a silane compound containing a polyfluoroalkyl group has been covered, faces the outside of the vehicle.

[0019] Further, this is the water repellent reflection reduction glass described above which is characterized by each oxide thin membrane of the aforementioned reflection reduction glass being formed using the sol-gel method in which more than one kind of organic metal compounds are used as the starting raw material.

[0020] Furthermore, this is the water repellent reflection reduction glass described above which is characterized by the SiO₂ thin membrane or the mixed oxide thin membrane of SiO₂ and other oxides, on the surface of which a silane compound containing a fluoroalkyl group has been covered, being made by first forming the SiO₂ thin membrane or the mixed oxide thin membrane of SiO₂ and other oxides on the surface of a glass substrate at a treatment temperature of more than 400°C, and thereafter, coating, or coating and drying the silane compound containing the polyfluoroalkyl group onto the said oxide thin membrane surface at a temperature of less than 400°C.

[0021] Further, this is the water repellent reflection reduction glass described above which is characterized by the aforementioned oxides which mix with SiO₂ being whichever of or a mixture of TiO₂, ZrO₂, Al₂O₃, B₂O₃, SnO₂, In₂O₃, and TaO₃.

[0022] Also, this is to present the water repellent reflection reduction glass described above which is characterized by the aforementioned oxide thin membrane layers formed on the surface of the glass substrate being 2 or 3 layers. And further, this is the water repellent reflection reduction glass described above which is characterized by the uppermost layer of the aforementioned oxide thin membrane layers being the same membrane as the SiO₂ thin membrane or the mixed oxide thin membrane of SiO₂ and other oxides which was formed on the side opposite the said oxide thin membrane layer.

[0023] As mentioned before, as for the SiO_2 or the mixed oxide of SiO_2 and other oxides, it is preferred that its construction possess very fine concave and convex or small pores and that it be made so as not to lose its characteristic by increasing the surface dimensions of the membrane by forming fine concave and convex or fine pores which are sufficiently fixed possessing a unique shape and unique size on the surface layer, increasing the attachment weight of fluorinated material in such a way so as to bond the silane compound containing polyfluoro group which demonstrates water repellence, oil repellence, and soiling preventive properties in a single to a few tens of molecular layers to not simply the surface but also onto the interior of the pores, and making the silane compound containing the polyfluoro group sufficiently last a long period of time against surface rubbing from wiping.

[0024] Also, the concave/convex and fine pores formed on the surface layer possess sizes which are less than the wavelengths in the visible light zone and do not lose the see-through property in itself; further, the silane compound containing the polyfluoroalkyl group coated onto them possesses no color and is transparent, and its refractive index is as low as about 1.33 ~ 1.35 due to the polarization index of the fluorine atom being small, and because it is less than that of the low refractive index oxide material membrane, it is a single to a few tens of molecular layers, it is thin, and it is not that where the see-through property of the water repellent reflection reduction glass is lost from these treatments.

[0025] Also, the other oxide materials which are mixed with the SiO_2 means TiO_2 , Al_2O_3 , B_2O_3 , SnO_2 , In_2O_3 , or Ta_2O_5 , and especially, they can be selected freely among various oxides such as TiO_2 , ZrO_2 , Al_2O_3 , B_2O_3 , and SnO_2 ; it is best that the SiO_2 series oxide thin membrane, which is to be the uppermost layer, be formed using the sol-gel method where metal alcoxide is made the starting raw material, and it is necessary to select a mixed oxide material which is soluble with a SiO_2 series sol solution after mixing, becomes an uniformly mixed oxide sol solution, and further, at the time the thin membrane of the mixed oxide compound is formed, does not exceed a membrane refractive index of 1.50, preferably a refractive index of less than 1.47.

[0026] Also, as the silane compound containing the polyfluoroalkyl group, silane compounds containing a perfluoroalkyl group having a carbon number of 1 ~ 20 such as $\text{CF}_3(\text{CH}_2)_2\text{Si}(\text{OCH}_3)_3$, $\text{CF}_3(\text{CF}_2)_5(\text{CH}_2)_2\text{Si}(\text{OH})_3$, $\text{CF}_3(\text{CF}_2)_7(\text{CH}_2)_2\text{Si}(\text{OCH}_3)_3$, $\text{CF}_3(\text{CF}_2)_5(\text{CH}_2)_2\text{Si}(\text{OCH}_3)_2$, $\text{CF}_3(\text{CF}_2)_3(\text{CH}_2)_2\text{Si}(\text{OCH}_3)_3$, and $\text{CF}_3(\text{CF}_2)_7(\text{CH}_2)_2\text{SiCl}_3$, or condensates where they are hydrolyzed can be selected.

[0027] Also, as for the formation method of the aforementioned oxide thin material, for example, the formation method described in J.P. Hei. 3 - 316992 applied for by this applicant is the most suitable, and the said method uses a solution where the two kinds of precursor sols which possess different average molecular weights of, for example, a few 1,000s and a few 10,000s are mixed as the raw material solution of the oxide formed on the substrate, and an optional surface shape, for example, concave/convex or fine pores can be uniquely made simply by controlling the mix proportion.

[0028] Further, as a method to coat the aforementioned silane compound containing the polyfluoroalkyl group onto the aforementioned oxide thin membrane equipped with the aforementioned concave/convex or fine pores, there is, for example, the coating method described in J.P. Hei. 4 - 16688 previously applied for by this applicant; further there is that where low reflective glass made by laminating an oxide thin membrane is made based on a precise optical design, thereby sufficiently maintaining performance over a long period of time by providing water repellence and oil repellence to the unique surface equipped with durability which possesses a visible light low reflective performance from the beginning and where they have been made synergistically and totally unified.

[0029] That is to say, by making the low refractive index membrane of the oxide thin membrane which becomes the uppermost layer on the air side into the SiO_2 series oxide thin membrane (refractive index $n = 1.43 \sim 1.47$) which enables the lowest refractive index among the various oxide thin membranes to be obtained, it becomes that where one is able to drastically prevent and control the deterioration in the low reflection effect due to the attachment of soiling, which has been the fatal deficiency of conventional low reflective glass in manifesting the specified optical characteristic by forming the thickness of the membrane to a prescribed thickness based on the optical design while securing a low refractive index and surface layer formation control, which enables the aforementioned unique convex/concave and fine porous shapes to be obtained.

[0030] Also, as for the aforementioned glass substrate, it is transparent glass of an inorganic substance (organic in some cases), and it is not especially limited as to being colored or not colored and as for its kind and shape; further, needless to say, it can be used as a curved glass, as various membrane covered glasses, various reinforced and strengthened glasses, in a flat and single plate as well as multiple layer glass or bonded glass.

[0031] [Action]

As mentioned before, among those where a reflection reduction layer is installed by laminating oxide materials possessing differing refractive indexes onto one side of a glass substrate, the water repellent reflection reduction glass of this invention is formed with SiO_2 or a mixed oxide material of SiO_2 and other oxides of specified refractive index, with specified fluorinated material and with uniquely possessing fine concave and convex of a specified depth or fine pores of a specified diameter on the surface of the side opposite the said reflection reduction membrane layer side or on the uppermost layer of the said opposite side and the reflection layer, and it became that where its attachment property was improved and a firm thin membrane was made; the bonding of a membrane to another membrane at the laminated membranes boundaries is significantly improved, it possesses a sufficient see-through property, the reflection reduction effect is increased while it possesses water repellence, it is made so as to possess rubbing resistance and durability, it is transparent and high in hardness, it simultaneously manifests and sufficiently satisfies the specified optical characteristics, it provides a reflection reduction effect as well as water repellence, oil repellence, and soiling preventive properties, thereby controlling and preventing deterioration of the transparency, reflection lowering effect, and external appearance, it makes water and soils which cause the optical characteristic to be lost difficult to attach and it makes them be easy to wipe off by simply wiping even if they are attached, thus reducing the chances of surface scratching, it maintains excellent characteristics over a long period of time, and it can be obtained efficiently at low cost with a safe and uncomplicated processes, thereby making a useful water repellent reflection reduction glass which is widely used for building and vehicle windows.

[0032] [Practical Examples]

Below, this invention will be explained concretely based on the practical examples. However, this invention is not limited to these practical examples.

[0033] Practical Example 1

Ti alcoxide and Si alcoxide were mixed so as to become a mol ratio of oxide material conversion of about 43 : 57, a solvent such as isopropyl alcohol was added to this, and they were prepared so as to become a solution concentration of about 0.45 mol/l. The viscosity of the said alcoxide solution was about 2 mPa · s (cps).

[0034] Next, a float (phonetic) glass substrate possessing the size of a front glass of an automobile and a thickness of 2 mm (bronze color) was sequentially washed with a neutral washing agent, water rinse, alcohol, and acetone; after it was dried, one side of the said glass substrate was masked with masking tape and soaked in the prepared solution mentioned above, it was gently pulled up at a rate of about 3.0 mm/second thereby forming a gel membrane on the glass substrate, and thereafter, the masking tape was removed, and it was heat dried for 10 minutes in an electrical oven at a temperature of about 280°C. Thus, the first layer $\text{SiO}_2\text{-TiO}_2$ series oxide thin membrane was obtained.

[0035] Next, masking tape was once again pasted onto the non-membrane formed side of the glass substrate described above, it was soaked in a Si alcoxide solution possessing a viscosity of approximately 6 mPa · s which was prepared so as to become a solution concentration of about 0.25 mol/l, it was gently pulled up thereafter at a constant rate of approximately 4 mm/second, the masking tape was removed in a manner similar to the first layer, and it was heat dried again for 10 minutes at a temperature of 280°C. Thus, the second layer SiO_2 oxide thin membrane was obtained.

[0036] Next, a uniform silicasol solution was prepared possessing a solution concentration of about 0.4 mol/l in which silicasol (a) having an weight average molecular weight of about 126,000 where hydrolyzed-polycondensed tetraethoxysilane $[\text{Si}(\text{OH}_2\text{H}_5)_4]$ was made the starting raw material and silicasol (b) having an weight average molecular weight of about 3,200 where hydrolyzed-polycondensed monomethyltriethoxysilane $[\text{CH}_3\text{Si}(\text{C}_2\text{H}_5)_3]$ was made the starting raw material were mixed so as to become a mol ratio of oxide material conversion of 1 : 3.5. The viscosity of this solution was approximately 2.5 mPa · s.

[0037] A new glass substrate (clear) possessing a thickness of 2 mm and which was the same size as that which had been masked with masking tape was soaked into this solution, pulled up at a constant rate of about 4.5 mm/second, the masking tape was removed, and it was heat dried for 10 minutes at a temperature of about 280°C in the same electrical oven. Thus, an oxide thin membrane of SiO_2 on one side was obtained.

[0038] The two glass substrates so obtained were supplied to a front glass manufacturing line, and after they were cut to a specified shape, a heating process was performed having layered them in such a way so that the respective membrane formed sides of the said two glass substrates faced outward, and they were bent so that the membrane formed side of the bronze colored glass substrate became a concave plane and that of the clear color glass substrate became a convex plane.

[0039] A pair of the said multiple bent glass substrates for layered glass were taken out and cut into a small pieces, and the optical characteristics of each thin layer were measured; as a result, the laminated thin membrane layers on the bronze glass substrate was : the refractive index of the first thin membrane layer n_1 = approximately 1.75, the membrane thickness d_1 = approximately 100 nm of the SiO_2 - TiO_2 oxide thin membrane, the second thin membrane layer refractive index n_2 = approximately 1.45 and the thickness d_2 = approximately 118 nm of the SiO_2 oxide thin membrane. Also, the thin membrane layer formed on the clear glass substrate was : the refractive index n_1' = approximately 1.45 and the membrane thickness d_1' = approximately 120 nm.

[0040] Next, the remaining bent glass substrates for layered glass were separated, and about 10 cc of the solution in which the silane compound containing polyfluoroalkyl group was hydrolyzed was dropped using a dropper only onto the SiO_2 oxide thin membrane layer side, it was spread uniformly without unevenness using a cotton cloth, and thereafter, this clear glass substrate was heated for 30 minutes at a temperature of about 250°C in the aforementioned electrical drier oven. This formed a layer which was between a single molecular layer to a few tens of molecular layers.

[0041] Again, the said clear glass substrate and the bronze color glass substrate which were once separated were paired with a polyvinyl butyral membrane (PVB intermediary membrane) between the two glass substrates, and thereafter, a layered glass for front windows was obtained by placing them in an autoclave and pressuring and heating.

[0042] As the visible light reflective index of the concave side of the layered glass so obtained (the side facing the interior of the automobile when it was installed) was measured, the visible light reflective index of incident light possessing an incident angle of approximately 60° was about 9.3%. On the other hand, when the visible light reflective index was measured at an incident angle of about 60° with respect to ordinary front window layered glass of a combination of glass substrate where the thin layer mentioned above was not formed at all but which possessed the same PVB intermediary membrane thickness, it was about 15.4%. Accordingly, the layered glass which is the water repellent reflection reduction glass of this invention reduced the visible light reflective index by about 6.1%.

[0043] Also, when the contact angle with the water in the atmosphere on the convex side of the clear glass substrate of the said layered glass (the side facing the exterior of the car) was measured, it was about $110 \sim 115^\circ$ and a high water repellence was shown. Also, it was

excellent water repellent reflection reduction glass which could be wiped off easily in case of soils such as oil with alcohol without any trace being left.

[0044] Further, the said water repellence and oil repellence did not deteriorate over a long period, and this was water repellent reflection reduction glass which showed good results, for example, in a weatherability test based on an accelerated anti-weathering tester (Dew Panel Weathermeter) or in the 1,000 round oscillating motion test based on an approximately 1000 g/cm² rubbing test (traverse test) using a # 40 broad cloth.

[0045] Practical Example 2

A solution which was the same as that for the first thin membrane layer of Practical Example 1 was prepared, and a SiO₂-TiO₂ series oxide thin membrane was obtained as the first thin membrane layer by forming it by making the pull up rate from the said solution be about 3.2 mm/second.

[0046] Next, after Ti alcoxide and Si alcoxide were mixed at a mol ratio of oxide conversion so as to become 93 : 7, about 0.3% by weight of a solvent such as isopropyl alcohol and hydroxypropyl cellulose was added and mixed into this, and thus, a sol solution possessing a solution concentration of about 0.45 mol/l was prepared. The viscosity of the said solution was approximately 7 mPa · s.

[0047] Next, the said glass substrate where masking tape was once again masked on the non-membrane formed side of the glass substrate which formed the first thin membrane layer previously was soaked into the said solution, it was pulled up gently at a constant rate of about 2.8 mm/second, and it was heat dried for about 10 minutes in an electrical oven which was maintained at a temperature of approximately 280°C; thus, a SiO₂-TiO₂ series oxide thin membrane was obtained as the second thin membrane layer.

[0048] Further, the first thin membrane layer was formed on the said second thin membrane layer by performing the same work as was done in forming the first and the second thin membrane layers of Practical Example 1 except the pull up rate in the formation of the said third thin membrane layer was about 3.8 mm/second.

[0049] Using the glass substrate which formed the three layer laminated thin membrane layer so obtained and a clear glass substrate possessing water repellence which was obtained by performing the same work as was done in Practical Example 1, a layered glass for front windows was manufactured in the same manner as in Practical Example 1.

[0050] Also, as the optical measurements of the three layer thin membrane layer which was formed on the bronze color glass substrate were performed using the same operations as those for Practical Example 1, the first thin membrane layer was : the refractive index n_1 = approximately 1.75 and the membrane thickness d_1 = approximately 105 NM; the second thin membrane layer was : the refractive index n_2 = approximately 2.10 and the membrane thickness d_2 = approximately 135 NM; the third thin membrane layer was : the refractive index n_3 = approximately 1.45 and the membrane thickness d_3 = approximately 115 NM.

[0051] As the visible light reflective index of the concave side (the side facing the interior of the car) of the layered glass so obtained was measured in the same manner as with Practical Example 1, the visible light index of incident light at an incident angle of about 65° was approximately 13.8%. On the other hand, with respect to an ordinary front window layered glass possessing the same combination of substrates as stated above and possessing the same PVC intermediary membrane thickness but on which the aforementioned thin layer was not formed at all, as the visible light reflective index was measured at an incident angle of about 65° , it was about 19.9%. Accordingly, the layered glass which is the water repellent reflection reduction glass of this invention reduced its visible light reflective index by about 6.1%.

[0052] Also, as the contact angle of the convex side (the side facing the exterior of the car) with water in the atmosphere of the said layered clear glass substrate was measured, it was about $110 \sim 115^\circ$ and a high water repellence was shown. Also, against oil and soiling, it was capable of being wiped off extremely simply with, for example, alcohol; no traces were left, and it was found to be an excellent water repellent reflection reduction glass.

[0053] Further, it was an excellent water repellent reflection reduction glass which was equipped with the same water repellence, oil repellence, high weatherability, and anti-vibration properties.

Practical Example 3

After Zr alcoxide and Si alcoxide were mixed to become a mole ratio of oxide material conversion of approximately 67 : 33, a mixed solvent containing isopropyl alcohol and ethyl cellosolve was added to this and stirred, and an alcoxide solution possessing a solution concentration of about 0.3 mol/l was prepared. The viscosity of the said solution was about 2.5 mPa · s.

[0054] Next, a glass substrate having a thickness of 8 mm which was washed, sufficiently dried, and masked with masking tape was soaked in this solution, pulled up at a constant rate of about 3.0 mm/second, removed of the making tape, and heat dried for about 15 minutes in an electrical oven which was held at a temperature of about 350°C. Thus, a SiO_2 - ZrO_2 series oxide thin membrane was obtained as the first thin membrane layer.

[0055] Next, the above mentioned glass substrate was soaked without masking one side in the same solution in which the membrane was formed on a clear glass substrate in Practical Example 1, it was gently pulled up at a constant rate of about 4.5 mm/second, and it was heated for about 15 minutes at a temperature of about 350°C. Thus, a laminated thin membrane layer made of two layers on one side and a single layer thin membrane layer of one layer on the opposite side were formed on the glass substrate.

[0056] Next, the glass substrate so obtained was placed in a calcine oven and it was calcined for about 30 minutes at a temperature of about 550°C, it was gradually cooled, and thereby, a flat glass substrate where thin membrane layers were formed on both sides was obtained. Further, the water repellent solution used for Practical Example 1 was coated onto only the single layer thin membrane side of the glass substrate so obtained, and again this glass substrate was heated for about 20 minutes at a temperature of about 350°C.

[0057] As the optical measurements of the glass substrate so obtained were performed in the same manner as for Practical Example 1, the first thin membrane layer of the side formed with the two thin membrane layers was : the refractive index n_1 = approximately 1.75 and the membrane thickness d_1 = approximately 100 nm; the second thin layer membrane layer was : the refractive index n_2 = approximately 1.45 and the membrane thickness d_2 = approximately 120 nm; the opposite side single layer thin membrane layer was : the refractive index n_1' = approximately 1.45 and the membrane thickness d_1' = approximately 120 nm.

[0058] Further the visible light reflective index of incident light at an incident angle of 50° to the laminated thin membrane layer of two layers of the said glass substrate was about 5.3%, and in comparison, the visible light reflective index of a glass substrate at the same incident angle possessing the same thickness but without the formation of a thin membrane at all was 10.7%; this was a water repellent reflection reduction glass where its reflective index was reduced by approximately 5.4%.

[0059] Also, the side of the said glass substrate which was formed with a thin membrane layer of a single layer showed a contact angle with water in an atmosphere of the same $110 \sim 115^\circ$ as Practical Example 1 which was high water repellence, and this was a water repellent reflection reduction glass which showed a suitable characteristic for construction and show windows.

[0060] Comparative Example 1

In the aforementioned Practical Example 1, a laminated thin membrane layer of two layers formed onto the bronze color substrate and that where a thin membrane layer was not formed on a clear glass substrate, which becomes the other side of the layered glass, and where water repellent work in which silane compound containing polyfluoroalkyl group. such as described above are coated was not done were used, and a layered glass was produced.

[0061] The said layered glass had a visible light reflective index at an incident angle of 60° of about 11.4% and its reflective index was reduced by about 4.0% compared to about 15.4% for ordinary layered glass for front windows, but it was insufficient inasmuch as this was a reflective index reduction of about 2.1% less compared to the 6.1% reduction in the visible light reflective index for the layered glass of the water repellent reflection glass of this invention described Practical Example 1.

[0062] Comparative Example 2

In Practical Example 2, that where a laminated thin membrane layer of three layers was formed on a bronze color glass substrate and that where a thin membrane layer was not formed on a clear glass substrate which becomes the other side of the layered glass and where water repellent work was not performed in which a silane compound containing polyfluoroalkyl group such as those described above is coated were used, and a layered glass was produced.

[0063] The said layered glass had a visible light reflective index at an incident angle of 65° of about 16.0% and its reflective index was reduced by about 3.9% compared to about 19.9% for ordinary layered glass for front windows, but it was insufficient inasmuch as this was a reflective index reduction of 2.12% less compared to the 6.1% reduction in the visible light reflective index for the layered glass of the water repellent reflection glass of this invention described in Practical Example 1.

[0064] Comparative Example 3

In the aforementioned Practical Example 3, that where a laminated thin membrane layer of the same two layers was formed on one side of a glass substrate but where a thin layer was not formed on the masked opposite side had a visible light reflective index at an incident angle of 50° on the thin membrane layer side of about 7.2%, and this meant that it was lower in its performance by about 1.9% compared to Practical Example 3.

[0065] As mentioned above, based on the water repellent reflection reduction glass of this invention, a low reflection performance of a reflective index of $\pm 6\%$ at the attachment angle as a front window can be obtained, and it has a covering membrane possessing water repellent, oil repellent and soil resistance properties at a contact angle of 110 ~ 115°, it can be made inexpensively and effectively using simple and easy membrane formation steps, it demonstrates these performances exceptionally, it excels in water and oil repellence, soil resistance, bonding, rubbing scratch resistance, and weatherability without losing its optical characteristics which are maintained for a long period, it enables water and soil which have attached to be wiped off simply, and it is able to be suitably used in construction, automobile windows, and various glass products.

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(54)【発明の名称】 撥水性反射低減ガラス

(57)【要約】

【目的】 光学特性を損なうことなく、撥水撥油性と耐汚れ性を有し、反射低減を有しその性能をより格段に発揮するようにし、密着性、耐擦傷性ならびに耐候性等に優れ、長期に亘りその性能を保持し、水分や汚れが付着に対し簡単な払拭で充分対処できる、殊に自動車用窓材に有用な撥水性反射低減ガラスを得る。

【構成】 ガラス基板の片面に屈折率の異なる酸化物薄膜を積層しガラス面の反射を低減せしめた反射低減ガラスにおいて、該薄膜を積層した面と反対の面に、屈折率 n が1.50以下でかつポリフルオロアルキル基を含有するシラン化合物を少なくともその表面に結合させた SiO_2 薄膜もしくは SiO_2 と他の酸化物との混合酸化物薄膜を形成してなる撥水性反射低減ガラス。

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【特許請求の範囲】

【請求項1】 ガラス基板の片面に屈折率の異なる酸化物薄膜を積層しガラス面の反射を低減せしめた反射低減ガラスにおいて、該薄膜を積層した面と反対の面に、屈折率 n が1.50以下でかつポリフルオロアルキル基を含有するシラン化合物を少なくともその表面に結合させた SiO_2 薄膜もしくは SiO_2 と他の酸化物との混合酸化物薄膜を形成してなることを特徴とする撥水性反射低減ガラス。

【請求項2】 前記 SiO_2 薄膜もしくは SiO_2 と他の酸化物との混合酸化物薄膜の屈折率 n が、1.47以下であることを特徴とする請求項1記載の撥水性反射低減ガラス。

【請求項3】 前記ポリフルオロアルキル基を含有するシラン化合物が、単乃至数十分子層でなることを特徴とする請求項1乃至2記載の撥水性反射低減ガラス。

【請求項4】 前記撥水性反射低減ガラスが、少なくとも2枚のガラス基板を単なるあるいは各種機能性を有する中間膜または中間膜状物を介在して接着した合せガラスであることを特徴とする請求項1乃至3記載の撥水性反射低減ガラス。

【請求項5】 前記撥水性反射低減ガラスにおいて、前記積層した酸化物薄膜層が特定の入射角の入射光に対し、その反射率を最も低減せしめた薄膜層からなることを特徴とする請求項1乃至4記載の撥水性反射低減ガラス。

【請求項6】 前記撥水性反射低減ガラスにおいて、前記特定の入射角が $40^\circ \sim 80^\circ$ であって、その反射率の低減率が可視光反射率で4.5～7%であることを特徴とする請求項1乃至5記載の撥水性反射低減ガラス。

【請求項7】 前記撥水性反射低減ガラスにおいて、ポリフルオロアルキル基を含有するシラン化合物が少なくともその表面に被覆した SiO_2 薄膜もしくは SiO_2 と他の酸化物との混合酸化物薄膜が、屈折率 n が1.43～1.47で、かつ膜厚が105～130nmであることを特徴とする請求項1乃至6記載の撥水性反射低減ガラス。

【請求項8】 前記撥水性反射低減ガラスが、合せガラスでなる自動車用フロントウインドウであり、反射を低減せしめる酸化物薄膜層が車内面であり、ポリフルオロアルキル基を含有するシラン化合物が少なくともその表面に被覆した SiO_2 薄膜もしくは SiO_2 と他の酸化物との混合酸化物薄膜が車外面であることを特徴とする請求項1乃至7記載の撥水性反射低減ガラス。

【請求項9】 前記反射低減ガラスの各酸化物薄膜層が、少なくとも出発原料として有機金属化合物を1種以上含む溶液を用いるゾルゲル法で形成することであることを特徴とする請求項1乃至8記載の撥水性反射低減ガラス。

【請求項10】 前記ポリフルオロアルキル基を含有するシラン化合物が少なくともその表面に被覆した SiO_2 薄膜もしくは SiO_2 と他の酸化物との混合酸化物薄膜が、ガラス基板表面に一旦 SiO_2 薄膜もしくは SiO_2 と他の酸化物と

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の混合酸化物薄膜を 400°C 以上の処理温度で形成し、その後該酸化物薄膜表面にポリフルオロアルキル基を含有するシラン化合物を塗布もしくは塗布の後 400°C 以下の温度で乾燥し形成してなることを特徴とする請求項1乃至9記載の撥水性反射低減ガラス。

【請求項11】 前記 SiO_2 と混合する酸化物が、 TiO_2 、 ZrO_2 、 Al_2O_3 、 B_2O_3 、 SnO_2 、 In_2O_3 、 Ta_2O_5 のいずれかもしくはそれらの混合物であることを特徴とする請求項1乃至10記載の撥水性反射低減ガラス。

【請求項12】 前記ガラス基板の片面に形成する酸化物薄膜層が、2もしくは3層であることを特徴とする請求項1乃至11記載の撥水性反射低減ガラス。

【請求項13】 前記酸化物薄膜層の最上層が、該酸化物薄膜層の反対面に形成した SiO_2 薄膜もしくは SiO_2 と他の酸化物との混合酸化物薄膜と同一の膜であることを特徴とする請求項1乃至12記載の撥水性反射低減ガラス。

【発明の詳細な説明】

【0001】

【産業上の利用分野】 本発明は、車輛用、建築用あるいは一般産業用として用いられるガラス基板の片面の反射を低減せしめ、特に車輛用においては運転時のダッシュボードもしくはこれらの周辺部が特定傾斜角度で取り付けられたフロントガラスに対する映り込み現象を低減せしめる効果を持たせ、同時にその反対面（反射面）に、特に車輛用の車外面において撥水性能を持たせ、特に水分や汚れがその表面に付着しにくくなるような効果を少なくとも持ち合わせしめ、該膜に反射低減性能を有するようにならしめ、光学特性を損なうことなくその視野方向での透過性を増加せしめる、車輛においてことに安全性の向上に寄与する有用な撥水性反射低減ガラスを提供するものである。

【0002】

【従来の技術とその問題点】 従来から、例えばガラス基板上に屈折率の異なる酸化物膜を積層し、その多重干渉を利用してガラス基板の反射率を下げ透視性を改善し、車内の運転者や乗員はもとより対向車等に対しても、より安全性を有し、居住性に優れかつ環境に優しいものとなるものがより望まれるなかで、所謂多層膜低反射ガラスが知られており、実際に建築用、産業用あるいは車輛用等として広く用いられようとしてきている。

【0003】 特に、例えば自動車窓のうち、特定傾斜角度で取り付けられたフロントガラスに用いた従来の低反射性能では、正面からの反射光の低減を目的としたものであり、前記フロントガラス表面の垂直線（法線と以後いう）となす入射角が例えば $50^\circ \sim 70^\circ$ 以上の斜入射光に対しては、その低反射効果が半減するものであって、例えば運転車がダッシュボードもしくはそれらの周辺物がフロントガラスへの映り込みによって、ドライビング時における前景の視認性が低下し、安全性の低下等を発現

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することとなるものである。

【0004】これに対し、例えば特開平3-17601号公報には反射防止コーティングの形成方法が記載されており、また二層の反射防止膜を積層したものとして、例えば特開昭64-70701号公報には導電性反射防止膜を有する透明板が記載されており、さらに三層の反射防止膜を積層したものとして、例えば特開昭61-189501号公報には透明低反射板が記載されている等が知られている。

【0005】しかしながら、これら多層膜低反射ガラスでは、所望の光学特性を発現させるために屈折率と膜厚が厳密に計算されており、所定の膜構成を外れる場合には目標とする光学特性が得られなくなり、また低反射膜上に手垢、油、水垢などの汚れが付着した際にも、それらの汚れが低反射膜上に形成された新たな薄膜として作用することとなるため同様な問題を生じることとなる。

【0006】この際には、汚れが付着した部分は光学設計がずれ、周囲の正常な低反射部分に比べて反射率が上がり非常に目立ち易くなって、透視性や美観などを損ねることとなるものであった。

【0007】特に、指紋などの油性の汚れが付着した際には、アルコールなどの溶剤で払拭し完全に除去しない限り、いつまでも美観を損ねたままとなり易く、環境に優しいとは言い難く、また溶剤などの払拭跡も残り易いなどの種々の問題が発現することとなるものである。

【0008】上記の中で、例えば特公平3-23493号公報には防汚性を有する低反射率ガラスが記載され、ガラスの表面上に金属酸化物を含有する縮合体からなる屈折率1.60以上の薄膜と該薄膜上にフッ素原子が結合した炭素の数が2以上のポリフルオロカーボン鎖を有する含フッ素シリコン化合物の縮合体からなる薄膜との二層膜が形成されてなるものであることが開示されているものの、撥水性と低反射性を同時に得ようとして、F-アルキルシランとSi-アルコキシドを混合し、ハイブリッド化させた溶液を用いるものである。

【0009】

【発明が解決しようとする問題点】前述した例えば特開平3-17601号公報に記載されているように、ゾル・ゲル技術を用いてコーティングの厚みに対して軽金属弗化物の濃度勾配をもつコーティングを形成する方法は、複雑な作業工程を伴い、必ずしも高効率で生産性がよく経済的であるものとは言い難いものである。また例えば特開昭64-70701号公報ならびに特開昭61-189501号公報に記載されているものでは、前述した特定の斜入射光に対して、必ずしも充分かつ安定した所期の反射低減が得られ難いものであり、さらに該両者は必ずしも車輛用としての必要な耐久性があるものとは言い難いものである。

さらに例えば特公平3-23493号公報に記載されているものは、F-アルキルシランの分解を防ぐため、膜の最終加熱温度は400℃以下、例えば160～200℃程度にすることとなり、最上膜の硬度や強度が低いものしか

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得ることができないという問題がある。

【0010】さらに、ガラス基板の片面にのみ2～3層の酸化物薄膜層を形成した場合に発現される反射低減効果は4～6%の範囲であり、このままでも未処理のガラスに比べ非常に効果があるものであるが、可能であればさらに高い反射低減効果を発現できることが望ましい。しかしこのためには同一面にさらに薄膜層を積層させてもほとんど性能の向上は望めないばかりか、仮に1.0%以下の僅かな向上が見られる場合であっても、薄膜層の積層数が増加するに従い膜の耐久性が不十分であったり、薄膜層の均質性が低下して商品性が低下し易くなり、また製造工程も煩雑になりコストアップを招くことになる。

【0011】

【問題点を解決するための手段】本発明は、従来のかかる問題点に鑑みてなしたものであって、ガラス基板の片面にのみ2～3層の酸化物薄膜層を形成した場合に発現される反射低減効果を、同一面側への薄膜層の積層数を増やさずに増強するため、該薄膜層が形成される面と反対の面に、通常車輛用、建築用あるいは産業用に最も一般的に用いられるソーダライムシリケートガラスの屈折率 $n=1.51\sim1.53$ よりも低い屈折率1.50以下の薄膜を形成することによって、該2～3層の酸化物薄膜層を透過しガラス内に入射する光の反対面での反射（裏面反射ともいう）を低減させ、2～3層の酸化物薄膜層のみの場合に比べてさらに0.5乃至2.0%程度の性能向上を図るものである。そうしてまたさらに、その薄膜にフッ素原子を持つポリフルオロアルキル基を導入することによって水分や汚れの付着を防止する効果を持つようにさせ、反射低減効果の増強と撥水、汚れ防止効果とを併せ持った多機能となる撥水性反射低減ガラスを提供するものである。

【0012】すなわち、本発明は、ガラス基板の片面に屈折率の異なる酸化物薄膜を積層しガラス面の反射を低減せしめた反射低減ガラスにおいて、該薄膜を積層した面と反対の面に、屈折率 n が1.50以下でかつポリフルオロアルキル基を含有するシラン化合物を少なくともその表面に結合させた SiO_2 薄膜もしくは SiO_2 と他の酸化物との混合酸化物薄膜を形成してなることを特徴とする撥水性反射低減ガラス。

【0013】ならびに、前記 SiO_2 薄膜もしくは SiO_2 と他の酸化物との混合酸化物薄膜の屈折率 n が1.47以下であることを特徴とする上述した撥水性反射低減ガラス。ならびに、前記ポリフルオロアルキル基を含有するシラン化合物が、単乃至数十分子層でなることを特徴とする上述した撥水性反射低減ガラス。

【0014】さらに、前記撥水性反射低減ガラスが、少なくとも2枚のガラス基板を単なるあるいは各種機能性を有する中間膜または中間膜状物を介在して接着した合せガラスであることを特徴とする上述した撥水性反射低

減ガラス。

【0015】さらにまた、前記撥水性反射低減ガラスにおいて、前記積層した酸化物薄膜層が特定の入射角の入射光に対し、その反射率を最も低減せしめた薄膜層からなることを特徴とする上述した撥水性反射低減ガラス。

【0016】さらにまた、前記撥水性反射低減ガラスにおいて、前記特定の入射角が $40\sim 80^\circ$ であって、その反射率の低減率が可視光反射率で $4.5\sim 7\%$ であることを特徴とする上述した撥水性反射低減ガラス。

【0017】さらにまた、前記撥水性反射低減ガラスにおいて、ポリフルオロアルキル基を含有するシラン化合物が少なくともその表面に被覆した SiO_2 薄膜もしくは SiO_2 と他の酸化物との混合酸化物薄膜が、屈折率 n が $1.43\sim 1.47$ で、かつ膜厚が $105\sim 130\text{nm}$ であることを特徴とする上述した撥水性反射低減ガラス。

【0018】また、前記撥水性反射低減ガラスが、合せガラスでなる自動車用フロントウインドウであり、反射を低減せしめる酸化物薄膜層が車内面であり、ポリフルオロアルキル基を含有するシラン化合物が少なくともその表面に被覆した SiO_2 薄膜もしくは SiO_2 と他の酸化物との混合酸化物薄膜が車外面であることを特徴とする上述した撥水性反射低減ガラス。

【0019】またさらに、前記反射低減ガラスの各酸化物薄膜層が、少なくとも出発原料として有機金属化合物を1種以上含む溶液を用いるゾルゲル法で形成することであることを特徴とする上述した撥水性反射低減ガラス。

【0020】またさらに、前記ポリフルオロアルキル基を含有するシラン化合物が少なくともその表面に被覆した SiO_2 薄膜もしくは SiO_2 と他の酸化物との混合酸化物薄膜が、ガラス基板表面に一旦 SiO_2 薄膜もしくは SiO_2 と他の酸化物との混合酸化物薄膜を 400°C 以上の処理温度で形成し、その後該酸化物薄膜表面にポリフルオロアルキル基を含有するシラン化合物を塗布もしくは塗布の後 400°C 以下の温度で乾燥し形成してなることを特徴とする上述した撥水性反射低減ガラス。

【0021】またさらに、前記 SiO_2 と混合する酸化物が、 TiO_2 、 ZrO_2 、 Al_2O_3 、 B_2O_3 、 SnO_2 、 In_2O_3 、 Ta_2O_5 のいずれかもしくはそれらの混合物であることを特徴とする上述した撥水性反射低減ガラス。

【0022】また、前記ガラス基板の片面に形成する酸化物薄膜層が、2もしくは3層であることを特徴とする上述した撥水性反射低減ガラス。またさらに、前記酸化物薄膜層の最上層が、該酸化物薄膜層の反対面に形成した SiO_2 薄膜もしくは SiO_2 と他の酸化物との混合酸化物薄膜と同一の膜であることを特徴とする上述した撥水性反射低減ガラスをそれぞれ提供するものである。

【0023】ここで、前記したように、 SiO_2 もしくは SiO_2 と他の酸化物との混合酸化物としては、表面表層に微小な凹凸もしくは細孔を有する構造とすることが好まし

く、表面表層に特異な形状と特異な大きさとで充分強固な微小な凹凸もしくは細孔を形成せしめて膜の表面積を増やし、撥水性、撥油性ならびに汚染防止性を発現するポリフルオロ基含有シラン化合物を、単に表面に単乃至数十分子層に結合させるようにするだけでなく微小な凹凸もしくは細孔内部にも結合させるようにし、フッ化物の付着量を多くしてその機能を高めるとともに、さらに払拭などの表面の摩耗に対しても、前記ポリフルオロ基含有シラン化合物が充分長期に亘り残せ、それらの特性が損なわれることがないようにしたものである。

【0024】また、表面表層に形成した凹凸や細孔は、可視域の光の波長以下の大きさで、自体透視性を損なうものではなく、さらにこの上に塗布されるポリフルオロアルキル基含有シラン化合物は、無色透明であり、かつフッ素原子の分極率が小さいため屈折率が $1.33\sim 1.35$ 程度と低く、低屈折率酸化物膜以下でありかつ単乃至数十分子層であり、著しく薄いため、これらの処理によって撥水性反射低減ガラスの透視性を損なうことはないものである。

【0025】さらに、前記 SiO_2 と混合される他の酸化物とは、 TiO_2 、 ZrO_2 、 Al_2O_3 、 B_2O_3 、 SnO_2 、 In_2O_3 あるいは Ta_2O_5 など、ことに TiO_2 、 ZrO_2 、 Al_2O_3 、 B_2O_3 、 SnO_2 など種々の酸化物の中から適宜自由自在に選択することができるものであり、最上層となる当該 SiO_2 系酸化物薄膜を金属アルコキシドを出発原料とするゾルゲル法で形成することがよく、 SiO_2 系のゾル溶液と可溶性で混合後、均質な混合酸化物ゾル溶液となり、かつその混合酸化物の薄膜を形成した際に膜の屈折率が 1.50 を超えることがないような、好ましくは屈折率が 1.47 以下の混合酸化物を選択することが必要である。

【0026】さらにまた、前記ポリフルオロアルキル基を含有するシラン化合物としては、 $\text{CF}_3(\text{CH}_2)_2\text{Si}(\text{OC}(\text{H}_3)_3)_3$ 、 $\text{CF}_3(\text{CF}_2)_5(\text{CH}_2)_2\text{Si}(\text{OCH}_3)_3$ 、 $\text{CF}_3(\text{CF}_2)_7(\text{CH}_2)_2\text{Si}(\text{OCH}_3)_3$ 、 $\text{CF}_3(\text{CF}_2)_7(\text{CH}_2)_2\text{SiCH}_3(\text{OCH}_3)_2$ 、 $\text{CF}_3(\text{CF}_2)_3(\text{CH}_2)_2\text{Si}(\text{OCH}_3)_3$ 、 $\text{CF}_3(\text{CF}_2)_7(\text{CH}_2)_2\text{SiCl}_3$ 等のような炭素数が $1\sim 20$ のパーフルオロアルキル基を含むシラン化合物、もしくはこれらを加水分解した縮合体が採用できる。

【0027】またさらに、前記表面層形状を有する前記酸化物薄膜の形成方法としては、例えば本出願人が先に特願平3-316992号に記載した形成方法が最適であり、当該方法は、基板上に形成する酸化物の原料溶液として平均分子量が異なる、例えば数1000と数10万、2種類の前駆体ゾルを混合した溶液を用い、その混合の割合を制御することのみによって任意の表面層形状、例えば凹凸もしくは細孔、を特異に発現することができるものである。

【0028】またさらに、前記ポリフルオロアルキル基を含有するシラン化合物を、前記凹凸もしくは細孔を有する表面層形状を備えた前記酸化物薄膜上に塗布する方

法としては、例えば本出願人が先に出願した特願平4-16688号に記載した塗布方法であり、さらにこれらの方法を緻密な光学設計に基づき酸化物薄膜を積層して成る低反射ガラスとしたものであって、もともと可視光低反射性能を有する耐久性を備えた特異な表面層に、撥水・撥油ならびに耐汚染性を付与することとなり、相乗かつ総合的に一体となって長期に亘っても、その性能を充分発揮するものとなるものである。

【0029】すなわち、前記空気側の最上層となる酸化物薄膜の低屈折率膜を、種々の酸化物薄膜の中で最も低屈折率が得られる SiO_2 系酸化物薄膜（屈折率 $n=1.43\sim 1.47$ ）とすることによって、低屈折率と特異な前記凹凸や細孔形状が得られる表面層形状制御性とを確保しつつ、かつその膜厚を光学設計に基づいた所定の厚さに形成することによって所定の光学特性をも同時に発現させるため、従来低反射ガラスの致命的な欠陥であった汚れの付着による低反射効果の劣化を飛躍的に防止制御することが可能となったものである。

【0030】さらにまた、前記ガラス基板としては、無機質（場合によっては有機質）の透明板ガラスであって、無色または着色、ならびにその種類あるいは色調、形状等に特に限定されるものではなく、さらに曲げ板ガラスとしてはもちろん、各種被膜ガラス、各種強化ガラスや強度アップガラス、平板や単板で使用できるとともに、複層ガラスあるいは合せガラスとしても使用できることは言うまでもない。特に自動車用フロントウインドウに使用する合せガラスにおいて格段にその機能を発揮するものである。

【0031】

【作用】前述したとおり、本発明の撥水性反射低減ガラスは、ガラス基板上の片面に異なる屈折率の酸化物を積層して成る反射低減層を設けた中で、該反射低減層面の反対面あるいは該反対面と反射低減層の最上層に、例えば表面層に特定深さの微小な凹凸もしくは特定径の細孔を特異に有し、かつ特定の屈折率でかつ特定のフッ化物でなる SiO_2 もしくは SiO_2 と他の酸化物薄膜との混合酸化物でもって少なくとも形成することによるものであり、付着性も向上し頑固な薄膜とすることでき、ガラス基板との界面はもちろん、積層膜での膜と膜の界面においても密着性を格段に向上させ、撥水性を持たせつつ反射低減の効果を増大するようにして充分透視性があるかつ優れた耐摩耗性、耐久性を有するものとなり、透明で硬度が高い、しかも所定の光学特性等も同時に発現させて十分に満足できるものとでき、反射低減効果を付与すると同時に、撥水性、撥油性ならびに汚染防止性をも付与して、反射低減ガラスに特有の汚れの付着に起因する透視性の劣化、低反射効果の劣化ならびに美観の劣化を飛躍的に制御することができて防止することができ、光学特性を損なう水分や汚れが付着しにくく、しかも仮に付着しても極めて簡単に払拭によってこれらを除去でき、

さらに払拭などでの表面摩耗も低減しこれらの特性を損なうことが激減し、より長期に亘たりその優れた特性を維持できるものであるとともに、高安全で厄介な工程を必要とせず、安価に効率よく得られることとなって、建築用窓材にはもちろん車両用窓材等に、広く有用な撥水性反射低減ガラスとなるものである。

【0032】

【実施例】以下、実施例により本発明を具体的に説明する。ただし本発明に係る実施例に限定されるものではない。

【0033】実施例1

TiのアルコキシドとSiのアルコキシドとを酸化物換算のモル比で約43:57になるように混合し、これにイソプロピルアルコール等の溶媒を加えて溶質濃度約0.45mol/lに調製した。該アルコキシド溶液の粘度は約2 mPa·s (cps)であった。

【0034】次いで大きさが自動車用フロントガラスの素板サイズであり、厚さ約2mmのフロートガラス基板（ブロンズ色）を中性洗剤、水すすぎ、アルコール、アセトン等で順次洗浄し、乾燥した後、該ガラス基板の片面をマスキングテープでマスキングし、該ガラス基板を前記調製溶液中に浸漬し、約3.0mm/秒の一定速度で上方に静かに引き上げ、ガラス基板上にゲル膜を形成し、マスキングテープを取り除き約280℃に保持した電気炉中に約10分間入れ乾燥加熱し、第1層目の $\text{SiO}_2\cdot\text{TiO}_2$ 系酸化物薄膜を得た。

【0035】つぎに、上記ガラス基板の非成膜面に再度マスキングテープを貼り、溶質濃度約0.25mol/lとなるよう調整し粘度が約6 mPa·sであるSiアルコキシド溶液中に浸漬した後、約4mm/秒の一定速度で上方に静かに引き上げ、第1層目と同様にマスキングテープを取り除き、再度約280℃で約10分間保持乾燥加熱し、第2層目の SiO_2 の酸化物薄膜を得た。

【0036】さらに次いで、テトラエトキシシラン〔 $\text{Si}(\text{OC}_2\text{H}_5)_4$ 〕を出発原料とし、これを加水分解・重縮合させた重量平均分子量が約126,000のシリカゾル(a)と、モノメチルトリエトキシシラン〔 $\text{CH}_3\text{Si}(\text{C}_2\text{H}_5)_3$ 〕を出発原料とし、これを加水分解・重縮合させた重量平均分子量が約3,200のシリカゾル(b)とを、酸化物換算のモル比が約1:3.5となるように混合した溶質濃度約0.4mol/lの均一なシリカゾル溶液を調製した。この溶液の粘度は約2.5 mPa·sであった。

【0037】この溶液中に、片面を前記と同様にマスキングテープでマスキングした新たな前記同様のサイズで2mm厚さのガラス基板（クリアー）を浸漬し、上方に約4.5mm/秒の一定速度で静かに引き上げ、マスキングテープを取り除き、前記と同じ電気乾燥炉に入れて約280℃で約10分間加熱乾燥し、片面に SiO_2 の酸化物薄膜を得た。

【0038】得られた2枚のガラス基板を、自動車のフ

ロントガラスの製造ラインに供給し、同形の規定形状にそれぞれを切断した後、該2枚のガラス基板の成膜面がそれぞれ外側に向くように重ね、ブロンズ色のガラス基板の成膜面が凹面に、またクリアーのガラス基板の成膜面が凸面となるように曲げ加熱加工を行った。

【0039】得られた複数の該合せガラス用曲げガラス基板の中から1対を取り出し小片に切断し各薄膜層の光学特性を測定したところ、ブロンズガラス基板に形成した積層薄膜層は、第1薄膜層が屈折率 n_1 = 約1.75、膜厚 d_1 = 約100nmの $\text{SiO}_2 \cdot \text{TiO}_2$ 酸化物薄膜、第2薄膜層が屈折率 n_2 = 約1.45、膜厚 d_2 = 約118nmの SiO_2 酸化物薄膜であった。またクリアーガラス基板に形成した薄膜層は屈折率 n_1' = 約1.45、膜厚 d_1' = 約120nmであった。

【0040】次に、残りの合せガラス用曲げガラス基板を一旦再度別々に分離し、クリアーガラス基板の SiO_2 の酸化物薄膜層側のみに、ポリフルオロアルキル基を含有するシラン化合物を加水分解させた溶液をスポイドで約10cc滴下し、ネル布でむらなく均一に塗り広げ、さらにその後このクリアーガラス基板を前記乾燥電気炉に入れ、約250℃で約30分間乾燥加熱した。なお単分子層乃至数十分子層の間にある層を形成していた。

【0041】さらに再度、該クリアーガラス基板と、先に一旦分離した相手方のブロンズ色ガラス基板とを、該2枚のガラス基板の間にポリビニルブチラル膜(PVB中間膜)を挟持させベアリングした後、オートクレーブに入れ加圧加熱を行い、フロントウインドウ用の合せガラスを得た。

【0042】このようにして得られた合せガラスの凹面側(自動車窓として取り付け際車内面側)の可視光反射率を分光光度計で測定したところ、入射角約60°の入射光に対する可視光反射率が約9.3%であった。一方前記したような薄膜層を全く形成していないガラス基板の組み合わせは前記と同じであってかつPVB中間膜の厚みも同じである通常のフロントウインドウよう合せガラスについて、同様に入射角約60°での可視光反射率を測定したところ、約15.4%であった。したがって本発明の撥水性反射低減ガラスである合せガラスは、可視光反射率が約6.1%低減したこととなった。

【0043】また該合せガラスのクリアーガラス基板側の凸面(自動車窓として取り付け際車外側となる面)における、大気中での水に対する接触角を協和界面科学製CA-A型を用いて測定したところ、約110~115°程度であって、高い撥水性を示した。また油脂等の汚れの付着の際も、アルコール等で極めて簡単に払拭が可能であり、アルコールの払拭跡も残らない、所期のめざす優れた撥水性反射低減ガラスであった。

【0044】さらに、該撥水・撥油特性は長期に亘り劣化するようなことが少なく、例えば促進耐候試験機(デュパネルウエザーメーター)による耐候性試験、あるいは#40のブロード布による摩耗試験(トラバース試

験、約100g/cm²荷重による1000回程度往復摺動テスト)等でも良好な撥水性反射低減ガラスであった。

【0045】実施例2

実施例1における第1薄膜層と同様の溶液を調製し、実施例1と同様のガラス基板を用い、該溶液からの引き上げ速度を約3.2mm/秒として形成し、第1薄膜層として $\text{SiO}_2 \cdot \text{TiO}_2$ 系酸化物薄膜を得た。

【0046】次にTiのアルコキシドとSiのアルコキシドとを酸化物換算のモル比が約93:7になるように混合した後、これにイソプロピルアルコール等の溶媒と、さらに約0.3wt%の微量のヒドロキシプロピルセルロースを加えてよく混合し、溶質濃度が約0.45mol/lのゾル溶液を調製した。該溶液の粘度は約7mPa·sであった。

【0047】次いで先に第1薄膜層を形成したガラス基板の非成膜面を再度マスキングテープでマスキングした該ガラス基板を該溶液中に浸漬し、約2.8mm/秒の一定速度で静かに引き上げ、マスキングテープを取り外し、約280℃に保持した電気炉中で約10分間加熱乾燥し、第2薄膜層として $\text{SiO}_2 \cdot \text{TiO}_2$ 系酸化物薄膜を得た。

【0048】さらに該第2薄膜層上に、実施例1の第2薄膜層を形成したと全く同じ操作を行い第3薄膜層を形成した。ただし該第3薄膜層を形成する際の引き上げ速度は約3.8mm/秒であった。

【0049】こうして得られた3層の積層薄膜層を形成したガラス基板と、実施例1と全く同じ操作をして得られた撥水性能を持つクリアーガラス基板とを用い、実施例1と同様にフロントウインドウ用の合せガラスを作製した。

【0050】なお、実施例1と同様の操作によって、ブロンズ色ガラス基板に形成した3層の薄膜層の光学測定を行ったところ、第1薄膜層が屈折率 n_1 = 約1.75、膜厚 d_1 = 約105nm、第2薄膜層が屈折率 n_2 = 約2.10、膜厚 d_2 = 約135nm、第3薄膜層が屈折率 n_3 = 約1.45、膜厚 d_3 = 約115nmであった。

【0051】このようにして得られた合せガラスの凹面側(自動車窓として取り付け際車内面側)の可視光反射率を実施例1と同様に測定したところ、入射角約65°の入射光に対する可視光反射率が約13.8%であった。一方前記したような薄膜層を全く形成していないガラス基板の組み合わせは前記と同じであってかつPVB中間膜の厚みも同じである通常のフロントウインドウよう合せガラスについて、同様に入射角約65°での可視光反射率を測定したところ、約19.9%であった。したがって本発明の撥水性反射低減ガラスである合せガラスは、可視光反射率が約6.1%低減したこととなった。

【0052】また該合せガラスのクリアーガラス基板側の凸面(自動車窓として取り付け際車外側となる面)における、大気中での水に対する接触角を実施例1と同様に測定したところ、約110~115°程度であって、高い撥水性を示した。また油脂等の汚れの付着の際も、アル

コール等で極めて簡単に払拭が可能であり、アルコールの払拭跡も残らない、所期のめざす優れた撥水性反射低減ガラスであった。

【0053】さらに、実施例1と同様、撥水・撥油性に對し高い耐候性、耐摺動性を備える、優れた撥水性反射低減ガラスであった。

実施例3

ZrのアルコキシドとSiのアルコキシドとを酸化物換算のモル比が約67:33になるように混合した後、これにイソプロピルアルコール：エチルセロソルブ等を含む混合溶媒を入れて攪拌し、溶質濃度が約0.3mol/lのアルコキシド溶液を調製した。該溶液の粘度は約2.5mPa・sであった。

【0054】次いでよく洗浄し充分乾燥させ、かつ片面のみマスキングテープで覆いマスキングした板厚8mmのガラス基板を該溶液中に浸漬し、約3.0mm/秒の一定速度で静かに引き上げ、マスキングテープを取り外し、約350℃に保持した電気加熱炉中で約15分間加熱乾燥し、第1薄膜層としてSiO₂・ZrO₂系酸化物薄膜を得た。

【0055】次に実施例1でクリアーガラス基板上に成膜したと同じ溶液中に、上記の該ガラス基板を片面マスキングを行わずに浸漬し、約4.5mm/秒の一定速度で静かに引き上げ両面に溶液を塗布し、約350℃で約15分間加熱し、ガラス基板に片面には2層からなる積層薄膜層、反対面に1層の単層薄膜層を形成した。

【0056】次いで得られたガラス基板を焼成炉に入れ、約550℃で約30分間の焼成を行い徐冷し、両面に薄膜層を形成したフラット形状のガラス基板を得た。さらにこうして得られたガラス基板の単層薄膜層側のみに、実施例1で用いた撥水性溶液を塗布し、再度該ガラス基板を約350℃で約20分間加熱した。

【0057】得られたガラス基板について実施例1と同様にして光学測定を行ったところ、2層の薄膜層を形成した側の第1薄膜層は屈折率 n_1 = 約1.75、膜厚 d_1 = 約100nm、第2薄膜層は屈折率 n_2 = 約1.45、膜厚 d_2 = 約120nmであり、反対面の単層の薄膜層は屈折率 n_1' = 約1.45、膜厚 d_1 = 約120nmであった。

【0058】さらに該ガラス基板の2層の積層薄膜層側への入射角50°の入射光に対する可視光反射率が約5.3%であり、薄膜を全く形成していない同じ厚みのガラス基板における同じ入射角での可視光反射率が10.7%に比し、反射率が約5.4%低減する撥水性反射低減ガラスであった。

【0059】また該ガラス基板の単層の薄膜層を形成した側は、大気中での水に対する接触角が実施例1と同じく110～115°で高い撥水性を示し、建築用やショーウィンドウ用等として好適な特性を示す撥水性反射低減ガラスであった。

【0060】比較例1

前記実施例1において、ブロンズ色ガラス基板に2層の積層薄膜層を形成したものをを用い、また合せガラスの相手となるクリアーガラス基板には薄膜層を形成せず、しかも上記のようなポリフルオロアルキル基を含有するシラン化合物を塗布する撥水操作を行わないものをを用いて合せガラスを作製した。

【0061】該合せガラスでは、入射角60°の可視光反射率が約11.4%であり、上記通常のフロントウィンドウ用の合せガラスの入射角60°での可視光反射率が約15.4%に比し、可視光反射率が約4.0%低下したが、実施例1の本発明の撥水性反射低減ガラスの合せガラスの場合の可視光反射率の低減率6.1%に比べ、2.1%程度の反射率低減効果が劣るものであり、不充分であった。

【0062】比較例2

前記実施例2において、ブロンズ色ガラス基板に3層の積層薄膜層を形成したものをを用い、また合せガラスの相手となるクリアーガラス基板には薄膜層を形成せず、しかも上記のようなポリフルオロアルキル基を含有するシラン化合物を塗布する撥水操作を行わないものをを用いて合せガラスを作製した。

【0063】該合せガラスでは、入射角65°の可視光反射率が約16.0%であり、上記通常のフロントウィンドウ用の合せガラスの入射角65°での可視光反射率が約19.9%に比し、可視光反射率が約3.9%低下したが、実施例1の本発明の撥水性反射低減ガラスの合せガラスの場合の可視光反射率の低減率6.1%に比べ、2.12%程度の反射率低減効果が劣るものであり、不充分であった。

【0064】比較例3

前記実施例3において、ガラス基板の片面に同様の2層の積層薄膜層を形成し、反対面にマスキングをして薄膜を形成しなかったものは、薄膜層側の入射角50°の可視光反射率が約7.2%であり、実施例3より1.9%程度その性能が低下したものであった。

【0065】

【発明の効果】以上前述したように、本発明の撥水性反射低減ガラスによれば、手軽に容易な膜形成手段でもって、フロントウィンドウの取付角度において6%前後以上の反射低減率である低反射性能と、接触角110～115°程度である撥水・撥油性および耐汚れ性を有する被膜を安価に効率よく得て、格段にその性能を発揮して、光学特性を損なうことなく、撥水撥油性、耐汚れ性、密着性、耐擦傷性ならびに耐候性等に優れ、長期に亘りその性能を保持し、水分や汚れが付着したとしても簡単な払拭で充分対処できるものとなる等、建築用もしくは自動車用窓材をはじめ、各種ガラス物品において好適に採用できる。